REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1, 1994	3. REPORT TYPE AND DATES COVERED

4. TITLE AND SUBTITLE

Supercritical Fluid Extraction: Preparing a Superior Mesophase Precursor for Carbon Fibers

5. FUNDING NUMBERS

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9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)

U. S. Army Research Office
P. O. Box 12211
Research Triangle Park, NC 27709-2211

94-30952

11. SUPPLEMENTARY NOTES

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12a. DISTRIBUTION/AVAILABILITY STATEMENT

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12b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

Supercritical fluid (SCF) extraction is being investigated for the production of mesophase pitch, the liquid-crystalline precursor for the manufacture of high-performance carbon fibers. The mesophase pitch is produced by fractionation of an isotropic petroleum pitch with supercritical toluene in a region of liquid-liquid equilibrium that exists at pressures above 40 bar. Dramatic improvements in the reliability of our apparatus have recently been made, and mesophase pitch can now be produced on a routine basis. An experimental program was conducted to explore the effects of temperature, solvent-to-pitch (S/P) ratio, and solvent solubility parameter on the properties of the mesophase pitch produced. Temperatures of 320 and 360°C, solubility parameters of 3.7 and 5.0 $(cal/cc)^{1/2}$, and S/P ratios of 2.5 and 3.5 were chosen to conform to a two-level, augmented factorial experiment. A linear model correlated the data to a high degree of certainty. Results indicate that we can adjust SCF operating conditions and tailor-make a mesophase pitch for a given end use. We have discovered a semitheoretical method for predicting *a priori* the softening point and yield of mesophase pitch for a given set of SCF operating conditions. The SCF extraction process can be represented on a pseudoternary phase diagram, and good estimates of product yields and softening points can be made from a limited experimental data measured at other conditions.

14. SUBJECT TERMS

mesophase pitch, supercritical fluid extraction, carbon fibers, petroleum pitch, toluene

15. NUMBER OF PAGES

11

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

AD-A284 933

SUPERCRITICAL FLUID EXTRACTION: PREPARING
A SUPERIOR MESOPHASE PRECURSOR FOR CARBON FIBERS

FINAL REPORT

MARK C. THIES

AUGUST 1, 1994

U.S. ARMY RESEARCH OFFICE

GRANT NO. DAAL03-92-G-0194

CLEMSON UNIVERSITY

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SUPERCRITICAL FLUID EXTRACTION: PREPARING A SUPERIOR MESOPHASE PRECURSOR FOR CARBON FIBERS

Statement of Problem

During the last ten years there has been an increasing interest in the development of composites for applications in the aerospace and electronics industries. Such materials take advantage of the rather unique properties of high-performance carbon fibers, such as high tensile strengths and very high thermal conductivities in the direction of the fiber. In fact, carbon fibers having tensile strengths four times that of steel and thermal conductivities three times that of copper have been manufactured [1]. The development of improved processes for the economical manufacture of high-performance carbon fibers is an important issue in the development of lower-cost advanced materials.

Petroleum pitch has considerable potential as a raw material for the production of economical high-performance carbon fibers. This material is an abundant carbonaceous product that is usually obtained by heat-soaking "decant oil", a by-product of the catalytic cracking of petroleum distillates. Untreated petroleum pitch has a randomly oriented, or isotropic, microstructure. Before being extruded into carbon fibers, this material must first be converted into a liquid crystalline, or mesophase pitch, whose highly ordered microstructure makes an important contribution to the final fiber properties.

Control of the mesophase pitch composition is very important, because the composition determines the liquid-crystal-forming ability, thermal stability, and rheological properties of the carbon fiber precursor. Unfortunately, present pitch treatment methods are limited in their ability to control the mesophase composition and result in less than ideal fiber properties.

Supercritical fluid (SCF) extraction is being investigated by our group for the production of mesophase pitch. Previous work indicates that this technique has the potential for producing a higher quality mesophase pitch at an economical cost.

Significant Results

Three major advances were made during the period of this research grant. First, process reliability was dramatically improved; we can now produce mesophase pitch by SCF extraction on a routine basis. Second, a comprehensive experimental design was carried out to explore the effects of SCF operating conditions on both the yield and physical properties of mesophase pitch. Third, a semitheoretical technique has been developed that can be used to predict product properties for a given set of operating conditions. Each of these accomplishments is discussed in detail below.

Improvement of Process Reliability. Although we first produced a mesophase pitch by SCF extraction in late 1991, at that time our apparatus was plagued with several problems that severely limited our ability to produce mesophase pitch in a reproducible and reliable manner. Significant modifications to the apparatus were made in the summer of 1992 to improve run-to-run reproducibility. A fugitive emission system was installed to condense, collect, and return all toluene vapors to their appropriate product vessels. A high-velocity static mixer and a centrifugal coil assembly were installed to ensure

that the toluene-pitch mixture attained equilibrium conditions [2]. As shown in the table below, toluene phase compositions from duplicate runs are now reproducible to better than ± 0.3 wt %.

Table I. Reproducibility of Experimental Runs

| Run No.* | T(°C) | P(bar) | S/P Ratio | Toluene Mass Extraction | |
				Bottom Phase	Top Phase
2a	320	46.5	3.5	0.239	0.844
2b				0.238	0.844
3a	320	94.1	2.5	0.245	0.742
3b				0.245	0.737
8a	360	154.7	3.5	0.183	0.802
8b				0.185	0.805
10a	340	83.7	3.0	0.230	0.801
10b				0.231	0.801

*same numbers, different letters indicate duplicate runs.

Although the above modifications solved our reproducibility problems, the apparatus at that time was still unreliable, i.e., it was subject to frequent breakdowns. However, in 1993 we made two discoveries that essentially solved our reliability problems. First, we discovered that continuously maintaining a high system pressure during the flushing of the system with decant oil prevents the accumulation of pitch residue in the cell. Dropping the system pressure for even a few seconds results in the precipitation of pitch in the cell. Once the pitch falls out of solution, it will not redissolve and quickly builds up to the point that the liquid-level indicator becomes inoperative. After this change in operating procedure, the cell remains clean and thus does not have to be serviced for months. The second discovery we made was that the bottom-phase fraction could be removed from the cell in a semicontinuous manner without having a deleterious impact on process operating conditions. With this change, we were able to replace the relatively fragile micrometering valve with a much sturdier regulating-type valve. Since this valve change has been made, less than 10% of our experimental runs have had to be shut down due to valve failure or plugged lines.

After making these modifications to the apparatus in the winter of 1993, the increase in productivity was dramatic. During the entire fall of 1992, only 2 data points for our experimental design (see below) were made. However, in the spring of 1993, 8 successful runs were made in only 35 days! Essentially no serious operating difficulties have occurred since that time, and today we can make between 2 and 3 experimental runs per week. In summary, then, we have accomplished one of the major goals of this research project: we have developed a SCF extraction process that can be used to produce mesophase pitch on a routine basis. Furthermore, the technology being used to produce this pitch is readily amenable to scale-up.

An Experimental Design. Next, an experimental program was conducted to explore the effects of temperature, S/P ratio, and solvent solubility parameter on the properties of the mesophase pitch produced. Temperatures of 320 and 360°C, solvent solubility parameters (δ) of 3.7 and 5.0 (cal/cc)$^{1/2}$, and S/P ratios of 2.5 and 3.5 were chosen to conform to a two-level, augmented factorial experiment [3]. The solvent solubility parameter was chosen as an independent variable in the experimental design because it provides a rational and simple way to ensure that the system exhibited liquid-liquid equilibrium at every set of operating conditions studied. Figure 1a shows the range of operating variables that was investigated, and Figure 1b shows the experimental data that were measured. The product yield is defined as the percentage of the feed pitch that is recovered as a mesophase-containing pitch fraction. The softening point of that fraction was measured after residual toluene had been removed by vacuum drying. The percent mesophase was measured by polarized light microscopy [4]. As can be seen in Figure 1b, dramatic variations in both the product yield (from 11 to 36%) and the softening point (from 203 to 319°C) of mesophase pitch fractions were observed.

The experimental data were used to develop a statistical model for predicting the softening point and product yield as a function of the solubility parameter and temperature [5]. A linear model correlated the data to a high degree of certainty. Results demonstrate that it is possible to produce pitches with the same softening point at different T and δ, and at different product yields. These results are exciting, because they illustrate the degree of control that one has on the production of mesophase pitch. Furthermore, they illustrate that SCF extraction is selective for certain kinds of pitch molecules.

Figure 2 shows a plot of percent mesophase vs. softening point for the bottom-phase fractions collected in the experimental runs. Samples with low softening points contain just a small percent of mesophase because too high a fraction of disordering, low molecular weight molecules remain in the bottom-phase. As a greater fraction of the feed pitch is extracted by the SCF solvent, the high molecular weight species concentrate in the bottom phase. As a result, the softening point increases and a higher percent of mesophase is formed. Of particular interest to us is the fact that several fractions containing 100% mesophase were produced, and these fractions have a wide range of softening points.

Thus, with SCF extraction, we can adjust the operating conditions and tailor a mesophase pitch for a given end use. For example, the lower-melting mesophases may be best for the matrix phase of a carbon-carbon composite, and the higher-melting for either high modulus or high thermal conductivity fibers. To our knowledge, such control of the softening point of a 100% mesophase pitch is impossible with conventional heat-soaking technology.

Prediction of SCF Extraction Operating Conditions. Although the statistical model that was developed from the experimental design (i.e., Figure 1) is useful, it has significant limitations. In particular, it does not advance our fundamental understanding of the SCF extraction process (i.e., it is completely empirical) and cannot be used to extrapolate outside of the "cube" shown in Figure 1.

Recently, however, we have discovered a semitheoretical method for predicting *a priori* the softening point and yield of mesophase pitch for a given set of SCF operating conditions. The key to our discovery was recognizing that, although pitch is a multicomponent system, essential features
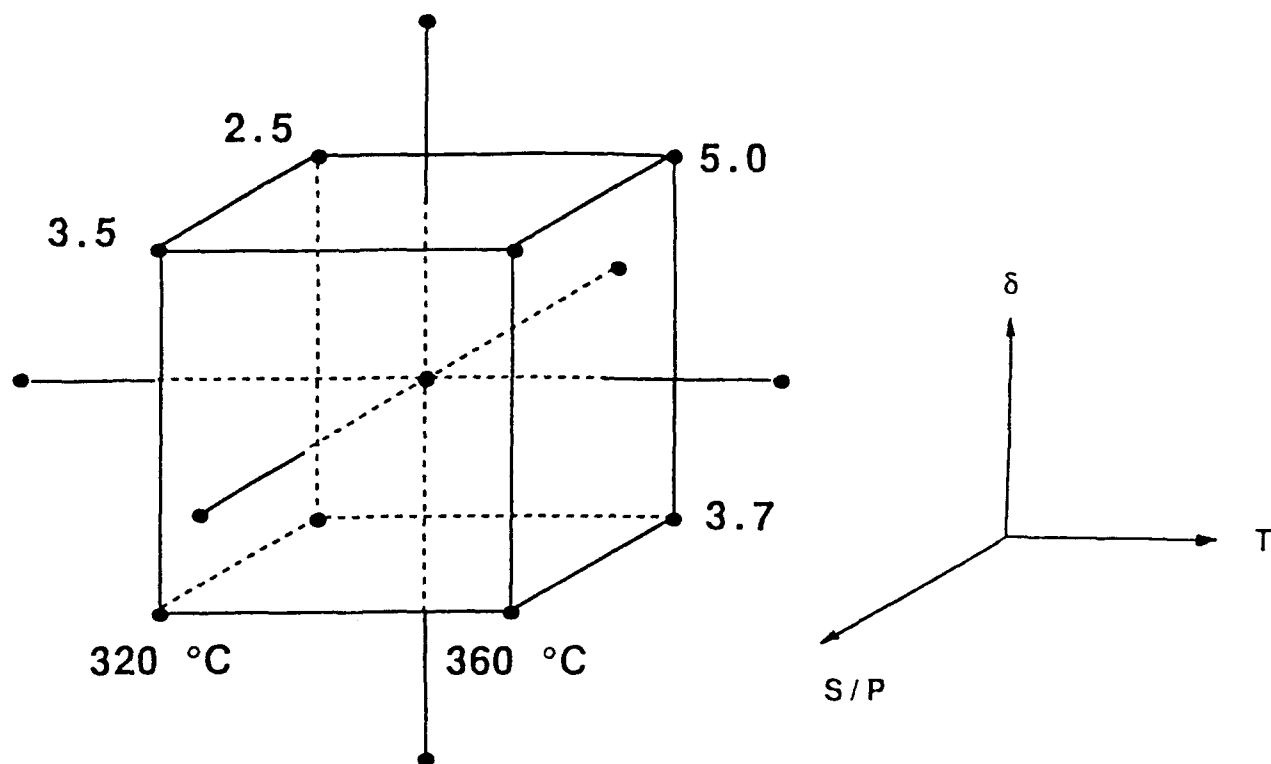
Figure 1a. Experimental design for exploring SCF extraction operating conditions.
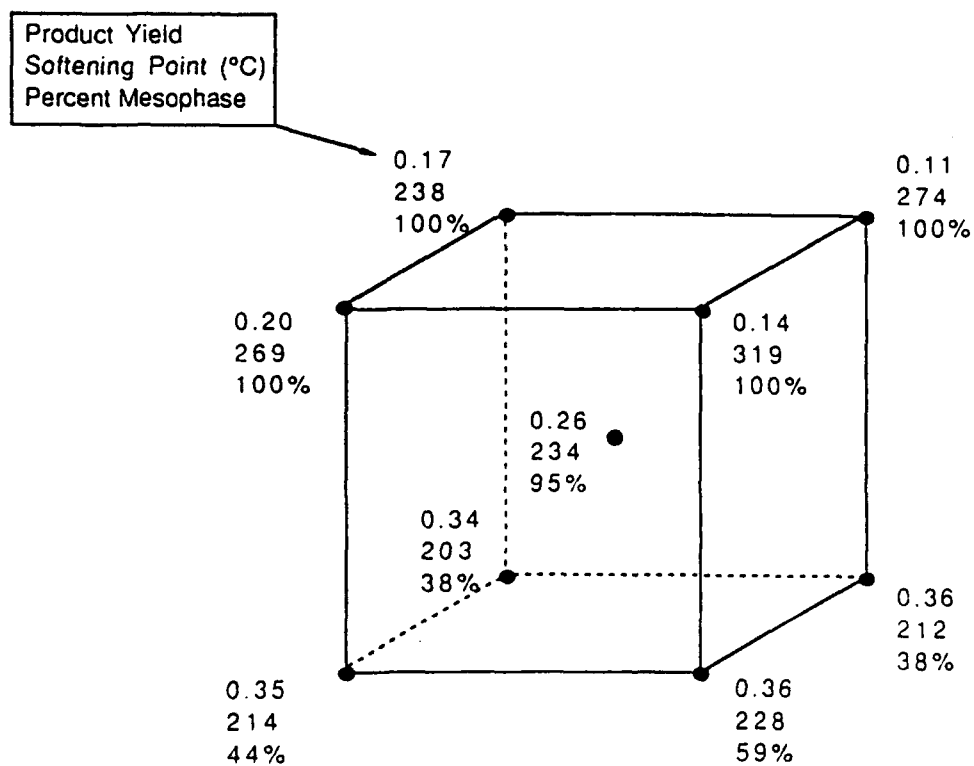

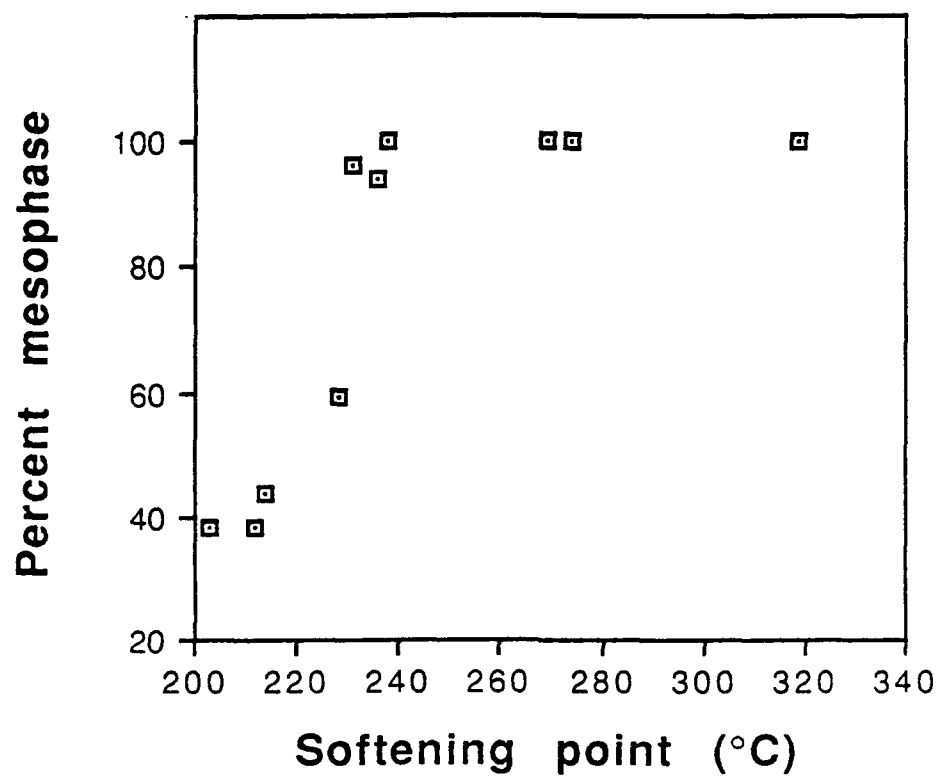**Figure 1b.** Results of our experimental runs.

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Figure 2. Percent mesophase vs. softening point for supercritically extracted mesophase pitches.

of the process can be quantified by assuming that the system only consists of 3 components: toluene, "light" pitch molecules, and "heavy" pitch molecules. Once that assumption has been made, we can represent the SCF extraction process on a ternary phase diagram. Only 2 variables on such a diagram are independent; thus, we chose the two variables measured for all of our experiments (wt% toluene in given phase and the softening point of the bottom phase) for plotting. The generation of such diagrams is discussed in many chemical engineering textbooks and must be done in a manner consistent with the Gibbs phase rule and with the material balance.

The ability of our technique to predict experimental data was tested in the following manner. First, all data from the experimental design (i.e., Figure 1) were plotted on ternary phase diagrams. As an example, the data at 320°C and a solubility parameter (δ) of 5.0 (cal/cc)$^{1/2}$, or P = 94.1 bar, are plotted in Figure 3. Several lines are plotted on the graph:

(1)   The equilibrium tie lines are located using the wt % toluene and softening-point results. For example, the endpoints of the upper tie line correspond to 22 wt % toluene and a softening point of 269°C in the bottom phase; the top phase contains 82% toluene.

(2)   The phase boundary curve is generated by drawing a smooth curve through the tie-line endpoints; this curve encompasses the liquid-liquid region. Outside of this curve only one liquid phase exists and pitch cannot be fractionated.

(3)   The feed line represents the mixing of the feed pitch and pure toluene. Its location satisfies the overall material balance such that the actual, measured S/P ratios and product yields are correctly reproduced. The intersection of the feed line with the upper tie line at 78.5% toluene corresponds to the experimental S/P ratio of 3.65:1 (i.e., $\frac{78.5}{21.5} = 3.65$). The product yield cannot be directly read off, but can be obtained by applying the lever rule to the tie lines. For example, the yield for the upper tie line is calculated to be 20%, in agreement with the product yield shown in Figure 1.

Now, according to the phase diagram that we have generated, increasing the S/P ratio will not affect the product yield significantly and will raise the bottom phase softening point. In contrast, decreasing the S/P ratio will reduce both product yield and softening point. These predictions were tested by making two additional experimental runs at 320°C and 94.1 bar (δ = 5.0): one at a S/P ratio of 2.1, and another at a S/P ratio of 3.70. As shown in Figure 4, the experimental results are in good agreement with the predicted results, with the new equilibrium tie lines lying close to the phase boundary curve that had been previously estimated using only 2 data points.

The analogous procedure to that described above for 320°C, δ = 5.0 was followed for the other 3 sets of T and δ shown in Figure 1. That is, diagrams were generated with the 2 available data points, predictions were made for 2 more data points, and these points were then experimentally measured. In all cases, the predictions and subsequent measurements were in good agreement. Furthermore, the S/P ratio at which bottom phase just begins to be formed (i.e., the phase boundary) was also correctly predicted [6].
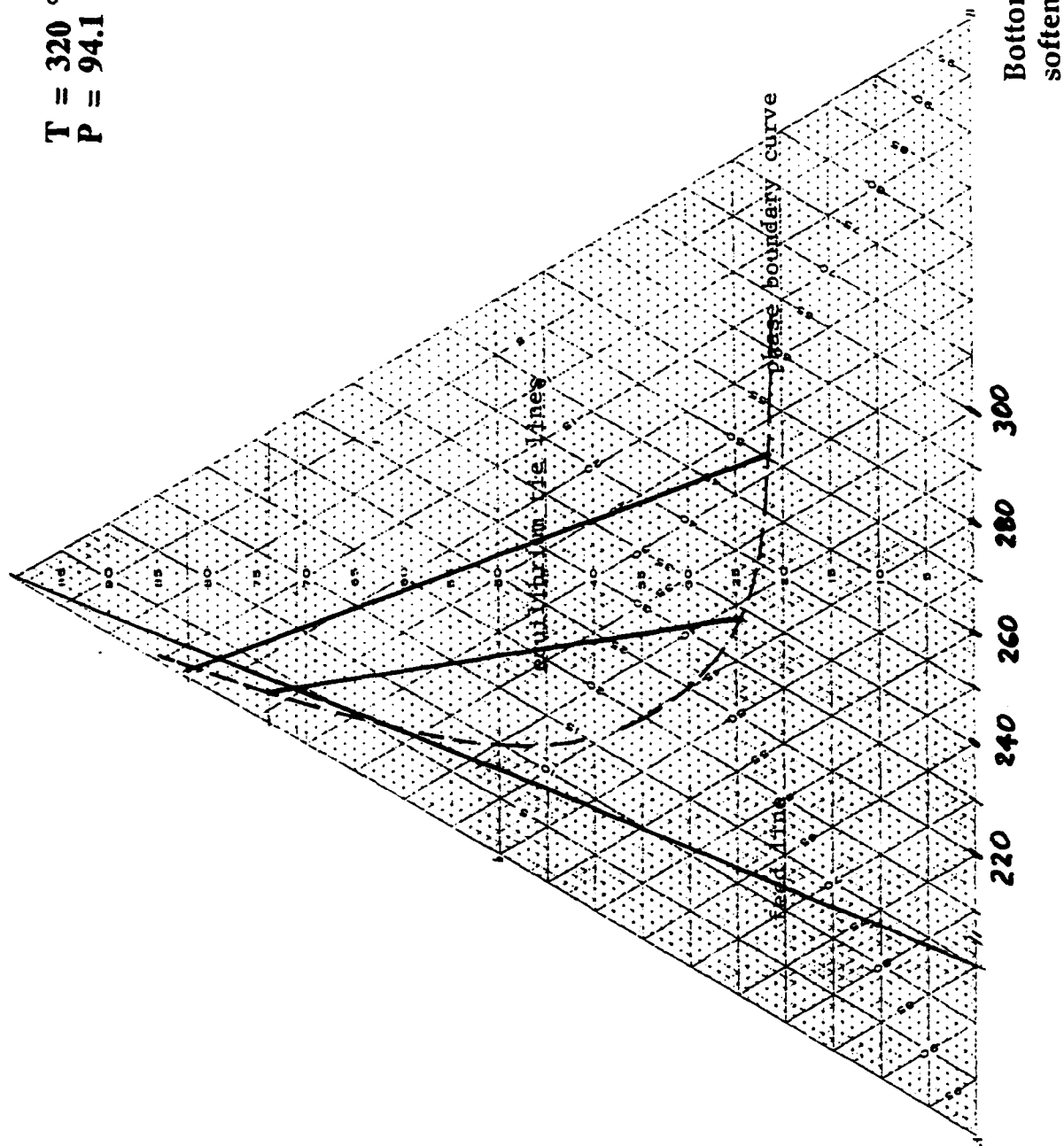
T = 320 °C
P = 94.1 bar

Toluene

Figure 3. Ternary phase diagram for SCF extraction of feed pitch at 320 °C, 94.1 bar, and two S/P ratios.
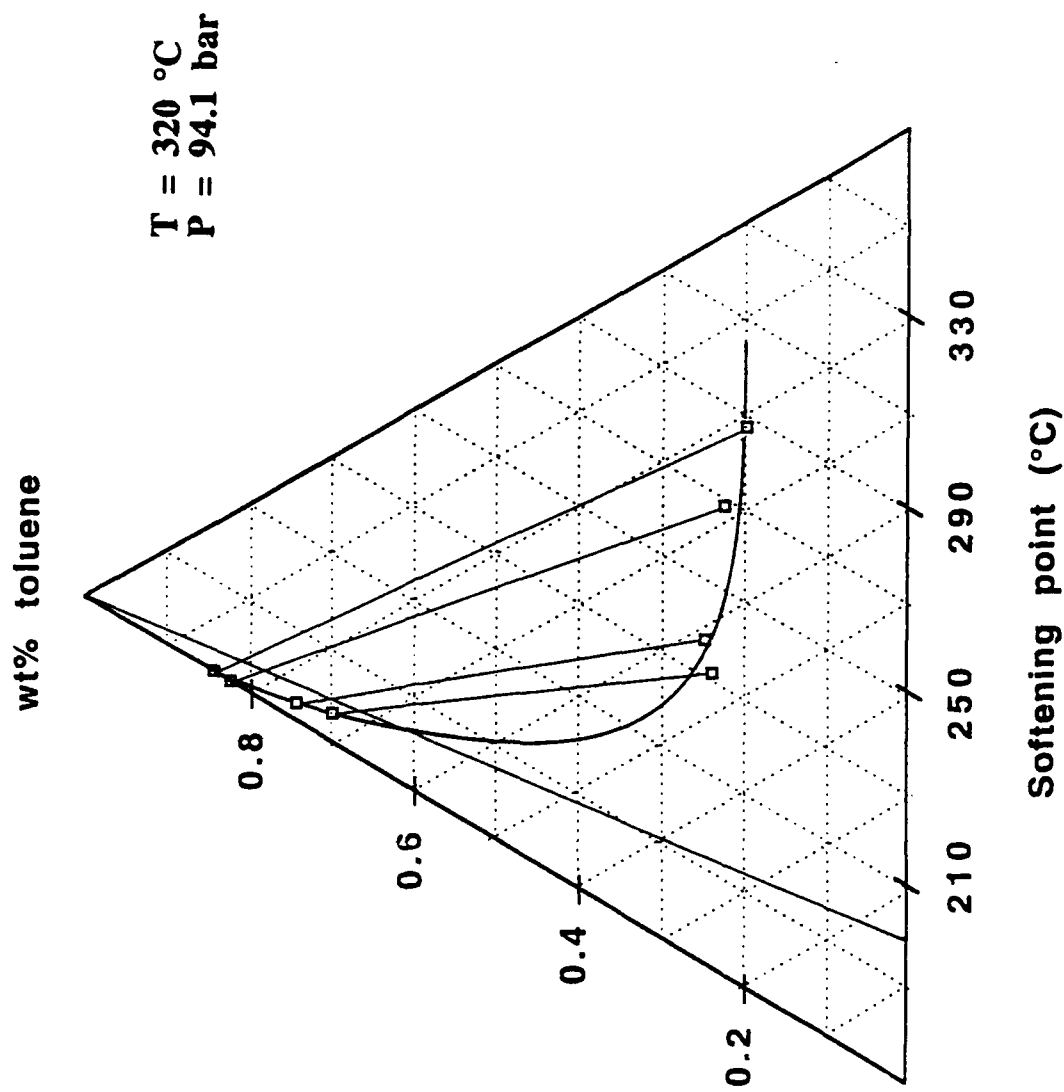
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Figure 4. Ternary phase diagram for SCF extraction of feed pitch at 320 °C, 94.1 bar, and four S/P ratios.

Although these diagrams are quantitatively correct only for the specific pitch being used, they can also be used to understand how changing the S/P ratio, the average molecular weight of the pitch, and the process T and P will affect mesophase pitch properties. We hope in future work to develop a more rigorous thermodynamic model for our process based on an equation of state [4], but we nevertheless believe that this new technique will be particularly useful if our process is commercialized, where it can be used to assist process optimization.

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4. Hochgeschurtz, T., Hutchenson, K. W., Roebers, J. R., Liu, G.-Z., Mullins, J. C., and Thies, M. C. Production of mesophase pitch by supercritical fluid extraction. Supercritical Fluid Engineering Science. Fundamentals and Applications; Kiran, E. and Brennecke, J. F., Eds. ACS Symposium Series 514. American Chemical Society: Washington, DC, 1993, 347-362.

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6. Bolaños, G. and Thies, M. C. Submitted to Journal of Supercritical Fluids, 1994.

List of Publications

1. Hochgeschurtz, T., Hutchenson, K. W., Roebers, J. R., Liu, G.-Z., Mullins, J. C., and Thies, M. C., "Production of Mesophase Pitch by Supercritical Fluid Extraction," Supercritical Fluid Engineering Science. Fundamentals and Applications; Kiran, E. and Brennecke, J. F., Eds. ACS Symposium Series 514. American Chemical Society: Washington, DC, 1993, 347-362.

2. Bolaños, G., Liu, G.-Z., Hochgeschurtz, T., and Thies, M. C., "Producing a Carbon Fiber Precursor by Supercritical Fluid Extraction," Fluid Phase Equilibria, 82, 1993, p. 303.

3. Bolaños, G., Davis, J. K., Liu, G.-Z., and Thies, M. C., "Production of Mesophase Pitch by Supercritical Fluid Extraction: An Exploration of Operating Conditions," Proceedings of the 21st Biennial Conference on Carbon, June 13-18, 1993, Buffalo, NY, p. 260.

4. Bolaños, G. and Thies, M. C., "Production of Mesophase Pitch by Supercritical Fluid Extraction: An Exploration of Operating Conditions," Presented at AIChE Spring National Meeting, Atlanta, GA, April 1994, paper 74c.

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